

Title (en)

Process for the preparation of gamma, delta-unsaturated ketones by Carroll-reaction, catalysts for this process and their preparation

Title (de)

Verfahren zur Herstellung Gamma, Delta-ungesättigter Ketone durch Carroll-Reaktion, neue Katalysatoren für dieses Verfahren und deren Herstellung

Title (fr)

Procédé pour la préparation de cétones gamma, delta-insaturées par la réaction Carroll, catalyseurs pour ce procédé et leur préparation

Publication

EP 0909750 B1 20020918 (DE)

Application

EP 98119215 A 19981012

Priority

- DE 19745672 A 19971017
- DE 19815810 A 19980408

Abstract (en)

[origin: EP0909750A1] Preparation of gamma, delta -unsaturated ketones (I) by modified Carroll reaction is catalysed by a stable liquid aluminum acetoacetate compound or mixture of such compounds. Some such catalyst mixtures are new. Preparation of gamma, delta -unsaturated ketones of formula (I) involves modified Carroll reaction of an allyl alcohol of formula (II) with diketene or an alkyl acetoacetate of formula (III) in presence of an aluminum catalyst. R1 = H or 1-20C, saturated or unsaturated, branched hydrocarbyl; R2 = 1-5C alkyl. The novelty is that the catalyst consists of an aluminum compound (or aluminum compound mixture) which is a stable liquid at room temperature and contains at least one alkyl acetoacetate-forming group and 1 or 2 alkoxy groups or exclusively alkyl acetoacetate forming groups which are esterified sec. butanol or isobutanol or with at least two different alkanols. Independent claims are included for: (1) new mixtures of aluminum tris-acetoacetates of formula (V) which are liquid at room temperature; and (2) the preparation of mixtures as in (1). R3 = 1-5C alkyl, preferably Me or Et; R4 = 3-10C alkyl, preferably CHMe2, CH(Me)Et, CMe3 or CH(Me)-C3H7; R5 = 1-10C alkyl, preferably Me, Et, CHMe2, CH(Me)Et or CH(Me)-C3H7; provided that R3-R5 are not all the same. A further Independent claim relates to the continuous preparation of compounds (V) (or their mixtures), having the narrower proviso that R3-R5 can only be the same if they are -CH(Me)Et or -CH2CHMe2, which are liquid at room temperature. The process involves continuously reacting 1 mole of aluminum alcoholate of formula (VI) with 3-10 moles of (III), or with at least 3 moles of a mixture of 2 or 3 different compounds (III), optionally dissolved in an inert solvent. Reaction is at 100-250 (preferably 150-200) degrees C and 1-100 (preferably 1-10) bars with a dwell time of 5-120 (preferably 15-45) minutes, the pressure and temperature being such that no gas phase is formed in the reaction vessel. R6 = 2-10C alkyl, preferably -CH2CHMe2, -CH(Me)Et or -CH(Me)C3H7; provided that R2 and R6 can only be the same if they are -CH(Me)Et or -CH2CHMe2.

IPC 1-7

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IPC 8 full level

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CPC (source: EP US)

B01J 31/0211 (2013.01 - EP US); **C07C 45/676** (2013.01 - EP US); **C07F 5/069** (2013.01 - EP US)

C-Set (source: EP US)

C07C 45/676 + **C07C 49/203**

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- GB 822572 A 19591028 - ROURE BERTRAND FILS ETS
- FR 2371411 A1 19780616 - BASF AG [DE]
- Chem. Abstr., AN 88:75419 & JP-A52112698 (21.09.1977)

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WO2017098048A1; WO0014046A1

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